Improving the field-emission properties of carbon nanotubes by magnetically controlled nickel-electroplating treatment*

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A novel magnetically controlled Ni-plating method has been developed to improve the field-emission properties of carbon nanotubes (CNTs). The effect of the magnetic field and Ni-electroplating on CNT field-emission properties was investigated, and the results are demonstrated using scanning electron microscopy, J–E and the duration test. After treatment, the turn-on electric field declines from 1.55 to 0.91 V/μm at an emission current density of 100 μA/cm^2, and the emission current density increases from 0.011 to 0.34 mA/cm^2 at an electric field of 1.0 V/μm. Both the brightness and uniformity of the CNT emission performance are improved after treatment.

Keywords: carbon nanotubes, magnetic field, field emission, Ni-electroplate

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1. Introduction

Due to special geometrical morphology, and properties including high aspect ratio, small tip radii of curvature, high current capacity, large field enhancement factor and high electrical conductivity, carbon nanotubes (CNTs) are ideal materials for efficient field emitters.[1−4] In recent years, many research studies have been performed on CNTs as field emission (FE) cathode materials.[5−8] In general, CNT FE cathodes could be made by different methods such as chemical vapour deposition (CVD),[9−11] screen-printing,[12,13] electrophoresis[14−16] and the spray method.[17,18] The direct growth of CNT FE cathodes using CVD usually has low-throughput, and the high growth temperature would limit the choice of substrate materials. The other methods can be carried out under low temperature and have the advantage of being low cost, simple processes. However, these methods usually have the problem of no CNT emitters vertical to the surface, which leads to the poor emission properties of CNTs.

There are many post-treatments used to improve the FE characteristics, such as adhesive taping,[19] soft rubber rolling,[20] focused ion beams,[21] plasma treatment,[22] and elastomers.[23] However, adhesive taping and soft rubber rolling lead to contaminants, and are limited to the simple diode-type cathode structure. Focused ion beam and plasma treatments require expensive instruments and complex proceedings, and the elastomer treatment leads to a residual elastomer.

In this paper, a simple and effective post-treatment based on magnetically controlled Ni-electroplating to erect the CNT emitters is presented. Not only does our method prevent residual pollution, but it also makes the CNT upright. As a result, the CNT emitters treated by the method show higher FE performance than those that were untreated.

2. Experiment

First, multi-walled CNTs (4g) with a diameter of 8–15 nm, a length of about 30 μm and a purity greater than 95% were dispersed in 1-L isopropyl alcohol solution containing 10 g/L dissolved polyvinylpyrrolidone (K30) by the ultrasonic cell crusher (model: SCIENT2-IID) at power equal to 2% for 10 min. Second, the preparation of the electrophoresis suspension,

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10 ml of the 4 g/L multi-walled carbon nanotubes (MWCNTs) suspension and 0.2 g $Mg(NO_3)_2{\cdot}6H_2O$, was added into the 1-L isopropyl alcohol solution for 60 min ultrasonic treatment. After that, the electrophoresis process was carried out. The graphite plate was used as the anode and the glass plate covered by Cr–Cu–Cr electrodes (produced by magnetic control sputter coaters) as the cathode; the distance between the cathode and the anode was 5 mm, and the voltage in the process was 12 V for 5 min. Third, the magnetically controlled Ni-electroplating process was carried out as depicted in Fig. 1(a): the electrophoretic prepared CNT electrodes were the cathode and the Ni plate was the anode; the distance between the cathode and the anode was 5 cm, and the magnitude of the square magnet beside the vessel was 1.2 T. The process was performed in a nickel sulphate bath with the following composition: 150-g/L $NiSO_4{\cdot}7H_2O$, 30-g/L $NiCl_2{\cdot}6H_2O$, 40-g/L H_3BO_3 and 0.1-g/L $C12H_{25}SO_4Na$. The treatment was carried out at 60 °C for 30 s at the current density of 1 mA/cm^2 with a pH value of about 5.4. Fourth, the cathode was dried in an oven at 200 °C for 20 min and sintered in an oven filled with 99.99% nitrogen at 500 °C for 30 min to remove the organic residue (such as the K30 in the electrophoresis process), and then cooled down to room temperature. Fifth, the Ni-electroplating CNT cathode was treated by the square magnet as depicted in Fig. 2 (the third, fourth and fifth steps of the experiment comprised the magnetically controlled Ni-electroplating treatment).

The morphologies of the CNT cathode were characterized by scanning electron microscope (SEM, S-3000 HITACH). The FE images of the samples were measured in conventional diode configuration, with the gap between the cathode and the anode 1100 μm, the pressure 5.0×10^{-4} Pa, the cathode area 5 cm×8 cm, and the DC voltage 1300 V. Indium tin oxide (ITO) glasses coated with green-phosphor were used as the anode.

3. Results and discussion

Figure 1 shows the magnetically controlled Ni-electroplating process. After the electrophoresis process, the cathode was covered by massive CNT. During the magnetically controlled Ni-electroplating process, the Ni plate was the anode and the cathode was the CNT-covered electrode. With a supply of current density at 1 mA/cm^2 for 30 s, the Ni particles travelled across the suspension to the cathode, went through the massive CNTs and attached onto the metal cathode.[24] Since the square magnet was on the left side, the travelling Ni particles were magnetically aligned on the cathode surface. According to the theory proposed by Fujiwara *et al.*,[25] when an external magnetic field is applied, the CNTs on the cathode are magnetized, as the deposition of the Ni particles on the cathode surface. As depicted in the enlarged view of the cathode in Fig. 1(b), the CNT attached to the cathode surface is polarized to negative, while the CNT tips are polarized to positive, which contributes to the magnetic alignment process of the CNTs.

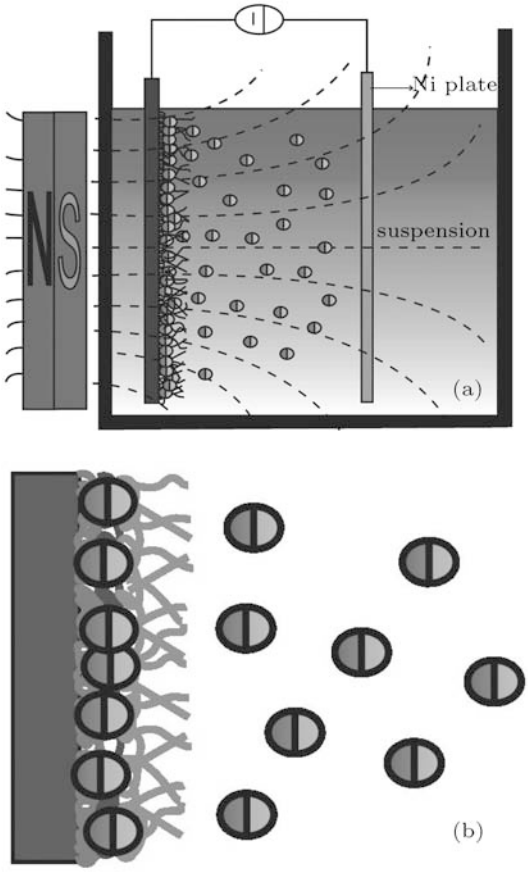


Fig. 1. (a) The magnetically controlled Ni-electroplating process, (b) an enlarged view of the cathode.

After the magnetically controlled Ni-electroplating process, the CNT cathode was dried in an oven at 200 °C for 20 min and sintered in an oven filled with 99.99% nitrogen at 500 °C for 30 min to remove organic residue, and then cooled down to room temperature. The CNT cathode was then placed beside the square magnet (magnitude 1.2 T) with a distance of 5 mm for 10 min, as depicted in Fig. 2. According to the theory proposed by Sharma *et*

al.,[26] with the supply of magnetic field, the nanotube tips, which had been polarized, became magnetized to saturation, behaved as a magnetic dipole, erected themselves from the surface, and then completed the alignment process. The electrical conduction nature of these aligned CNTs is dramatically improved in comparison with the randomly lying CNTs.

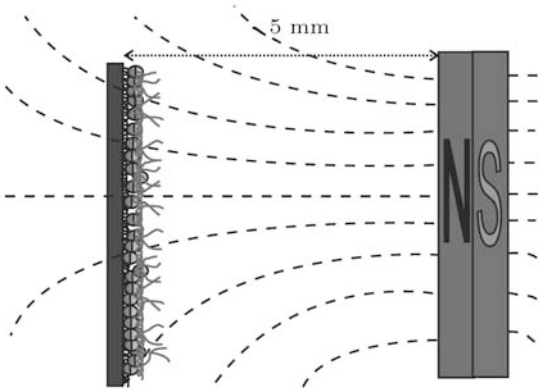


Fig. 2. The CNT cathode treated by the square magnet.

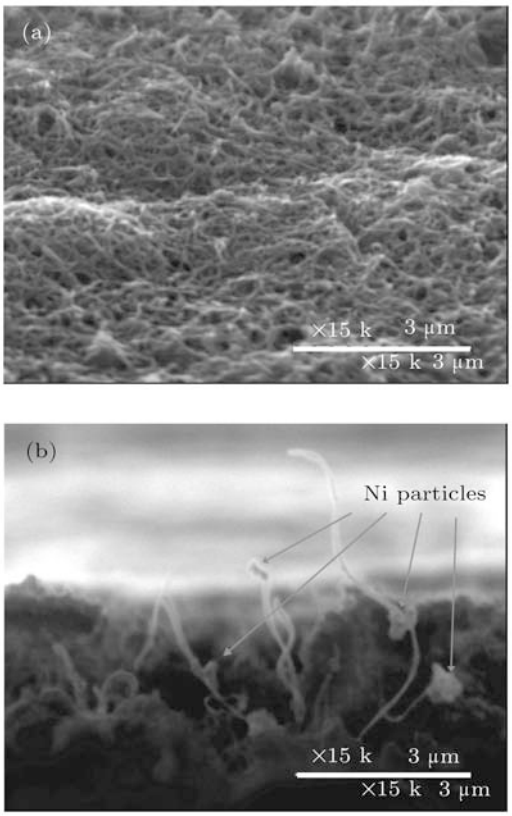


Fig. 3. The morphologies of the CNTs before (a) and after (b) magnetically controlled Ni-electroplating treatment.

The morphologies of the CNTs on the cathode before and after the magnetically controlled Ni-electroplating treatment were measured by SEM (S-3000 HITACH), and are shown in Fig. 3(a) and (b). In Fig. 3(a), almost all the electrophoretic deposited CNTs are laid on the surface, and it is difficult to find any MWCNTs vertical to the substrate. While in Fig. 3(b), there are obviously CNTs vertical to the surface due to the magnetically controlled Ni–CNT alignment process, and Ni particles accumulated on the CNT tip, body and substrate, which contribute to the magnetic alignment process.

From Fig. 4, the improvement in CNT FE characteristics before and after magnetically controlled Ni-electroplating treatment is clear: the turn-on electric field declines from 1.55 to 0.91 V/μm at an emission current density 100 μA/cm^2; and the emission current density increases from 0.011 to 0.34 mA/cm^2 at the electric field 1.0 V/μm. The FE of the treated and untreated specimens qualitatively follows the conventional Fowler–Nordhein (FN) theory, observed in Fig. 4 (inset). According to the FN equation, the emission current density is $J{=}A(\beta E)^2\exp(-B\varphi^{3/2}/\beta E)$, where A and B are constants, E is the applied electric field, φ is the work function and β is the field enhancement factor. Under the assumption that the work function φ of the CNTs is equal to that of graphite (5.0 eV), the field enhancement factor β after the magnetically controlled Ni-electroplating treatment is 3590, higher than the 1630 before the treatment.

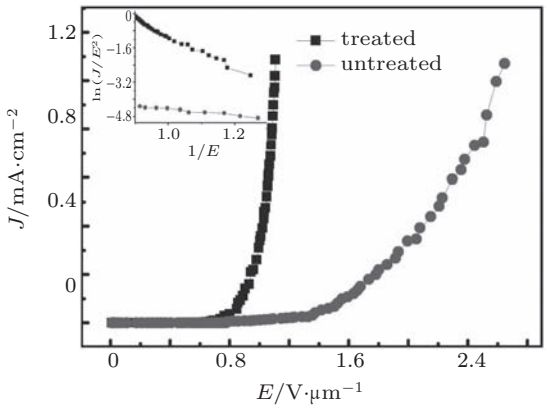


Fig. 4. Field-emission characteristics of the CNT emitters: I–V curve and FN plot (inset).

The FE images (both captured at exposure time 1/60 s and ISO:100) before and after the magnetically controlled Ni-electroplating treatment are shown in Fig. 5(a) and (b). It is clear that the treated one is brighter and more uniform than the untreated one. We assume three reasons for the improvement in CNT FE properties by magnetically controlled Ni-electroplating treatment. First, there are many CNTs

vertical to the cathode surface and so the FE characteristics will be greatly improved,[27] according to the theory proposed by Wang *et al.* Second, according to electro–magneto theory, the electric current gives rise to an electromagnetic field; the reason for the magnetization is the acceleration and conformity of the molecular current. After magnetic field alignment treatment, the electrons in the CNT material become more active and reach a higher Fermi level, which makes the FE easier than in the untreated ones. Third, on the one hand the electrons moving from the substrate to the vacuum follow the double-barrier model as shown in Fig. 6. The FE electrons tunnel through two barriers: first, electrons tunnel through barrier I between the CNTs and the substrate into the CNTs, then they tunnel through barrier II and are emmitted into the vacuum from the CNTs. On the other hand, the Ni particles electroplated on the substrate have good electrical conductivity, which contributes towards reducing barrier I. Therefore, with the Ni particles connecting the substrate and the CNTs, barrier I will be reduced and it is easier for the electrons to tunnel through barrier I between the CNTs and the substrate, which contributes towards an improvement in FE properties.

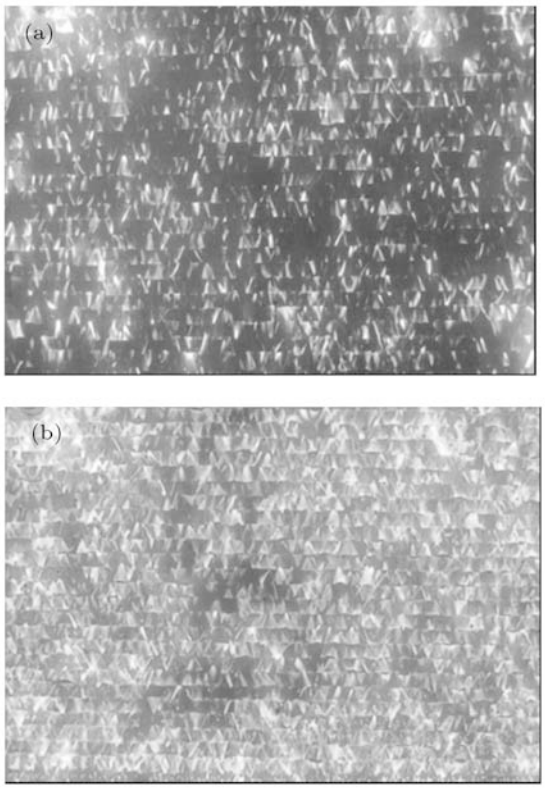


Fig. 5. Field-emission images of two specimens: before (a) and after (b) magnetically controlled Ni-electroplating treatment.

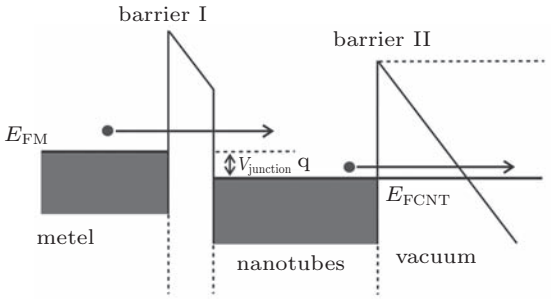


Fig. 6. The band structure of the double-barrier model for the field emission of the CNT film. E_{FM} and E_{FCNT} are the Fermi level of the substrate metal and the CNTs, respectively. $V_{junction}$ is the voltage dropped on the substrate–CNT junction.

In order to compare the degradation rate of the two cases, a lifetime measurement was performed for 20 h with a DC voltage of 1300 V. The initial current density of the two samples is about 1.121 and 0.021 mA/cm^2, respectively. As shown in Fig. 7(a), after 20 h the current density of the CNTs prepared by magnetically controlled Ni-electroplating treatment decreased to 75% of the initial current, whereas in Fig. 7(b) that of the CNTs without treatment dramatically decreased to 40% of the initial current, which means that the CNT emitters after magnetically controlled Ni-electroplating treatment had a longer duration than those that were untreated. Generally,

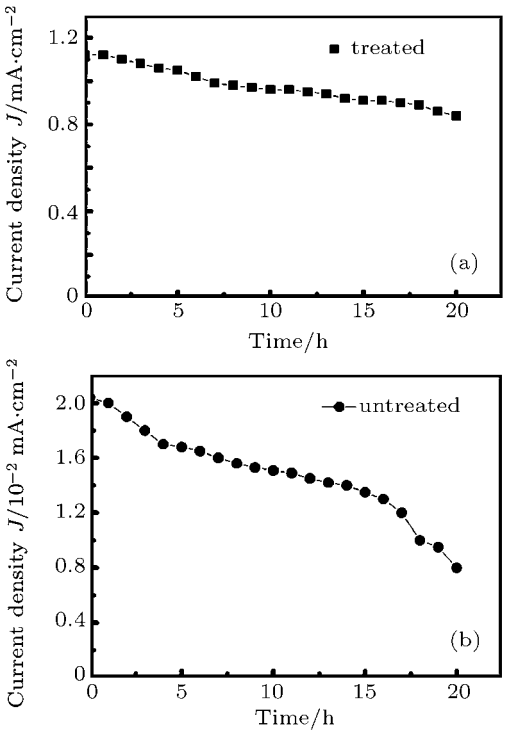


Fig. 7. Field-emission stability test of the two cases: treated (a) and untreated (b) by magnetically controlled Ni-electroplating treatment.

the emission current of CNTs decreases when residual gas molecules are adsorbed by Joule heating under a strong electric field.[28] The magnetically controlled Ni-electroplating treatment is advantageous at high vacuum, since there are no organic vehicles as the primary out-gassing sources in the electroplating suspension, unlike the electrophoresis suspension containing polyvinylpyrrolidone (K30). It is therefore confirmed that the above magnetically controlled Ni-electroplating treatment is facile and effective.

4. Conclusion

This work demonstrates that most CNTs on the cathode are magnetically erected to the surface by the magnetically controlled Ni-electroplating treatment. The FE properties of the CNTs are improved, the brightness and uniformity of the CNT diode configuration are promoted. Magnetically controlled Ni-electroplating treatment is facile and effective in FE display applications.

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